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Photo-induced Production of Chlorine Molecules from Titanium Dioxide Surfaces Containing Chloride

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Abstract: Titanium dioxide (TiO_2) is extensively used with the process of urbanization, and potentially influence the atmospheric chemistry, yet unclear. In this work, we demonstrated strong production of Cl_2 from illuminated KCl-coated TiO_2 membrane, and suggest an important daytime source of chlorine radicals. We found that water and oxygen were required for the reactions to proceed and Cl_2 production increased linearly with the amount of coated KCl, the humidity of carrier gas and the light intensity. These results suggested that water promotes the reactivity of coated KCl via the interaction with the crystal lattice to release free chloride ions (Cl^-). The free Cl^- transfer charge to O_2 via photoactivated TiO_2 to form Cl_2 and probably O_2^- radical. In addition to Cl_2, ClO

and HOCl were also observed via the complex reactions between Cl/Cl_2 and HO_x. An intensive campaign was conducted in Shanghai, during which evident daytime peak of Cl_2 was observed. Estimated Cl_2 production from TiO_2 photocatalysis can be up to 0.2 ppb/h, which were significantly higher than the photolysis of $ClNO_2$ and highly correlated to the observed Cl_2. Our results suggest a non-negligible role of TiO_2 in atmospheric photochemistry via altering the radical budget.

INTRODUCTION

Titanium dioxide (TiO_2), as the best photocatalyst, has been widely used in environmental remediation[1] and construction materials[2, 3]. The utilization of active TiO_2 for self-cleaning[4-6] or purifying atmospheric pollutants[7] increased significantly with the process of urbanization in recent years. These TiO_2-containing materials, as well as the TiO_2-containing particles such as dust[8] and combustion particles[9] can play increasing role in the atmospheric chemistry[10-13]. For example, the TiO_2 induced heterogeneous photochemical processes can promote the formation of several atmospheric oxidants, including HONO[14, 15], O_3[11], possibly NO_3[8, 16].

Atmospheric Cl radical, known as produced from the photolysis of Cl_2 and nitryl chloride ($ClNO_2$), is an important atmospheric oxidant[17], and influence the ozone and secondary aerosol formation[18-20]. Although concentrations of Cl radicals are typically lower than those of other atmospheric radicals, they can react with most atmospheric volatile organic compounds (VOCs) faster than hydroxyl radical (OH)[21] and therefore play an important role in the atmosphere[19], especially in coastal[22] and polluted urban areas[20, 23, 24]. The source of $ClNO_2$ is generated via the heterogeneous reaction of nitrogen pentoxide (N_2O_5) with particulate chloride[25]. However, there is no consensus on the main sources of Cl_2[17, 26]. Although it is traditionally believed that Cl_2 should decrease after sunrise due to its fast photolysis, several recent observations have reported evident daytime peaks of Cl_2, suggesting a considerable source of light-activated reactions[27-29] and possible contribution from photochemical sources. Herein, we report the first direct laboratory observation which confirms that TiO_2-mediated

photocatalytic reactions lead to the production of Cl_2, and a few other chlorinated species.

MATERIALS AND METHODS

Sample preparation. A suspension with 50 ml of KCl solution and 0.1 g of TiO_2 (Sigma-Aldrich, 21 nm primary particle size, ⩾99.5% trace metals basis, product number: 718467) was prepared to homogeneously coat KCl on TiO_2 particles. The TiO_2 particles in the suspension were then filtrated onto a 50 mm quartz membrane using a water vacuum pump. The membranes were then dried at 323 K before being used in the experiment. Samples with KCl/TiO_2 mass ratios of 0.0003 g/g, 0.0006 g/g, 0.003 g/g, 0.0057 g/g, 0.015 g/g, 0.028 g/g and 0.06 g/g were prepared. The amount of KCl coated on TiO_2 was measured by ion chromatography. A photo of a prepared sample is shown in Fig. S1.

Laboratory experiments. Fig. S2 shows a schematic of the experimental setup of a flow reactor system. The temperature of the system is kept at 293 K. Ultrapure air and nitrogen were used as the carrier gas, which was separated into a dry air flow and a wet air flow. The RH of the inflow to the reactor was adjusted by changing the ratio of dry air to wet air. Four UV lamps were mounted close to the tube, two of which (1 and 2) are used in all the experiments with irradiance of 16.3 W/m^2, except for the experiment testing the role of light intensity. The spectrum of the UV lights is shown in Fig. S3. The irradiance increased from 8.4 to 35.1 W/m^2 from one lamp to four lamps, which covered realistic ranges of solar UVA irradiance during the Shanghai campaign (Fig. S4). The temperature and RH inside the flow tube were monitored continuously. Three instruments, namely, a methyl iodide chemical ionization mass spectrometer (I-CIMS), a NO_x analyzer and an O_3 analyzer (Text S1), were used to measure Cl_2 and related species in the outflow from the tube. Four experiments were conducted during the lab campaign, and in each of them we varied a single experimental parameter, including coated KCl amounts, RH of the carrier gas, light irradiance and carrier gas types.

RESULTS AND DISCUSSION

Photo-induced production of Cl_2 from KCl-coated TiO_2. The main conclusion of the abovementioned experiments is that significant production of Cl_2 occurred in the presence of UV irradiation of a KCl-coated TiO_2 membrane. As shown in Fig. 1, we observed a strong production of Cl_2, up to 4-5 ppbv, from an irradiated sample, of which the KCl/TiO_2 ratio was 0.028 g/g and the RH of the carrier gas was 66%. The decrease in Cl_2 concentration indicated fast consumption of the coated KCl. The blank was obtained in many reference experiments, including using a blank membrane, a pure TiO_2 sample and a pure KCl sample, all of which did not show a noticeable increase of Cl_2. This confirms that Cl_2 was produced from the illuminated TiO_2 surfaces containing chloride.

A series of experiments were repeated with varying conditions to investigate the underlying mechanism of Cl_2 production and its dependence on potentially relevant parameters. An experiment testing the role of the amount of KCl coated on TiO_2 was carried out under three different RH values of 9.6%, 38% and 66%, representing very dry to slightly wet environments. The result at 66%, a more atmospherically relevant value, is shown in Fig. 2a. The results at the other RH values are shown in Fig. S5. The observed Cl_2 concentration increased linearly as the KCl/TiO_2 ratio increased from 0.0003 g/g to 0.0057 g/g and reached a plateau thereafter (Fig. 2a). The differences in both the production efficiency and saturated concentrations of Cl_2 among RH values of 9.6%, 38% and 66% were within the experimental errors, indicating that water is not a limiting factor in atmospherically relevant conditions.

Fig. 3 shows a comparison of Cl_2 production among different carrier gases, namely, dry nitrogen gas, wet nitrogen gas (RH = 38%), dry air and wet air (RH = 9.6%). Cl_2 cannot be observed with nitrogen carrier gas under both dry and wet conditions; instead, it is observed only in the system with wet air as the carrier gas. These results suggest that both water and oxygen are required in the reactions. To further investigate the potential role of water in the reaction, a humidity gradient experiment was conducted by changing the RH of the carrier gas from 0% to 88%. Similar to the dependence on the amount of coated KCl, the Cl_2 concentration increased linearly with the RH before

reaching a plateau (Fig. 2b), indicating that water is either a reagent or a factor influencing the activity of the reagent (chloride).

Free Cl^- are believed to be necessary in the reactions to provide electrons to the valence band of photoactivated TiO_2. KCl can form crystals of $(KCl)_6(H_2O)_n$ with very little water and release free Cl^- from the edge of the crystal lattice. This separation could be promoted by the number of water molecules, as solvent-shared ion pairs $[K^+(H_2O)Cl^-]$ are formed with 3-9 water molecules, whereas solvent-separated ion pairs (K^+ and Cl^-) can be observed with 10-15 water molecules[30]. This behavior explains why water can promote the reaction at a value much lower than the deliquescence RH of KCl. Cl_2 production would be determined by both the intensity of illumination and the amount of free Cl^-, which is influenced by both KCl and water. Under certain light irradiance, Cl_2 production will be linearly dependent on the level of free Cl^- (either KCl or water) before reaching a plateau where Cl_2 production is saturated and limited by the irradiance (Fig. 2a and 2b).

To test whether the observed plateau for Cl_2 production is due to the limitation of light irradiance and the relationship between them, we carried out an experiment in which the light number was adjusted from 4 to 1. The results showed that the concentration of Cl_2 produced linearly correlated with the light number and can reach greater than 10 ppbv (Fig. 2c), suggesting that the observed plateau of Cl_2 concentration in both the RH and coated KCl experiments is due to the Cl^- being saturated under a fixed light irradiance (2 UV lights, 16.3 W/m^2).

In addition to Cl_2, we also observed the production of ClO and HOCl under 66% RH, which showed similar dependence on the amount of coated KCl as did Cl_2 (Fig. 2d). The results of 38% RH are shown in Fig. S5. ClO is another important halogen radical in the atmosphere, while HOCl can be photolyzed to an OH radical and a Cl radical. ClO is typically believed to be formed via the reaction of Cl radical and O_3 in the atmosphere, which however, was not observed during the experiment, indicating an alternative pathway via the reaction of Cl radical and HO_2 radical to form ClO. Since

HO_x has been demonstrated to be produced from the photolysis of water on the surface of TiO_2[31-33], the reactions of Cl/Cl_2 with HO_x were thus suspected as the most likely pathway of forming ClO. HOCl can be produced from either the reaction of Cl_2 and OH or the reaction of ClO and HO_2. Note that HOCl could react with Cl^- ions to re-produce Cl_2. However, the concentration of HClO was too low (more than one order of magnitude) to explain the observed Cl_2 concentration.

In summary, we observed strong production of Cl_2 and moderate production of ClO and HOCl from the photo-induced reaction on KCl-coated TiO_2. A mechanism is proposed as the follows. Water reacts with KCl to release free Cl^-, which act as the donor to provide the electron to O_2 via the conduction and valence bands of photoactivated TiO_2 and form Cl radical and O_2^- radical[34]. Two Cl radicals combine to form the main product, the Cl_2 molecule. Water is photolyzed to OH and H^+, which react with O_2^- immediately to form HO_2 radicals. The produced Cl_2 further reacts with OH radical to form HOCl. Cl radical reacts with HO_2 to produce ClO radical. Most of the products from this reaction pathway are important atmospheric oxidants (or precursors of oxidants) and thus have the potential to influence atmospheric chemistry.

$$TiO_2 + hv \rightarrow h^+ + e^-$$

$$Cl^- + h^+ \rightarrow Cl\cdot$$

$$H_2O + h^+ \rightarrow OH\cdot + H^+$$

$$O_2 + e^- \rightarrow O_2^-\cdot$$

$$O_2^-\cdot + h^+ \rightarrow HO_2\cdot$$

$$Cl\cdot + Cl\cdot \rightarrow Cl_2$$

$$Cl_2 + hv \rightarrow Cl\cdot + Cl\cdot$$

$$Cl\cdot + HO_2\cdot \leftrightarrow ClO\cdot + OH\cdot$$

$$Cl_2 + OH\cdot \rightarrow HOCl + Cl\cdot$$

$$ClO\cdot + HO_2\cdot \rightarrow HOCl + O_2$$

$$HOCl + hv \rightarrow Cl\cdot + OH\cdot$$

Atmospheric Implication. In this study, we demonstrated a photo-induced reaction that can produce Cl_2 and in turn influence the atmospheric oxidative capacity by

forming Cl radical and ClO radical. The role of these reactions in the real atmosphere depends primarily on whether there are considerable amounts of chloride-coated TiO_2 materials exposed to the atmosphere. With the process of modern urbanization, TiO_2 containing materials have been widely applied for building exteriors[35] (Fig. S7), self-cleaning glasses, road lamps, airport roofs, and road bricks[31], and easily be exposure to the urban atmosphere. To further identify the role of the above mentioned reactions in the atmosphere, we tested some commercial TiO_2-containing materials, including anatase type TiO_2, rutile type TiO_2, self-cleaning glass, photocatalytic spray and white pigment. Most of these materials except rutile type TiO_2 can produce Cl_2 with different efficiency (Fig. S8).

In an area like East China where had elevated concentration of atmospheric chloride[36] (Fig. S9) and increased application of TiO_2 photocatalytic materials[29], the chloride chemistry involving TiO_2 may play an important role in the atmospheric chemistry. We conducted a field campaign in the city center of Shanghai, the largest city in China (Fig. 4), to measure the reactive chlorine compounds, including Cl_2 and $ClNO_2$ using an I-ToF-CIMS, and HCl and Cl^- using an online IC system (MARGA). Cl_2 revealed an evident daytime peak, which cannot be explained by the photolysis of $ClNO_2$ and indicate a missing ubiquitous daytime source of Cl_2. We calculated the production of Cl_2 from TiO_2 involving reactions with the assumption of 0% - 20% of the land surfaces covered by TiO_2-containing materials in urban Shanghai. Estimated Cl_2 production rate from TiO_2 photocatalysis can be up to 0.2 ppb/h (see Text S3), which were significantly higher than the photolysis of $ClNO_2$ and highly correlated to the observed Cl_2 (R^2=0.97). These results confirmed an important role of TiO_2 involved chlorine chemistry in the atmosphere. However, we can't ensure that this uncertainty range, and need some more statistic collection work get more details about urban usage of TiO_2. With the establishment of emerging cities and the use of photocatalytic environmentally friendly materials, this factor may be even higher in the future.

ASSOCIATED CONTENT

Supporting Information

A photo showing the prepared sample of KCl coated TiO_2 (Figure S1). The schematic of the experimental setup of a flow reactor system (Figure S2). Light spectra of the UV lamb (Figure S3). Diurnal variation of UVA during the Shanghai campaign (Figure S4). Dependence of the Cl_2 concentration as a function of the amount of coated KCl with the RH of carrier gas at (a) 9.6%, and (b) 38% (Figure S5a and b); (c) Dependence of the ClO and HOCl as a function of the amount of coated KCl with the RH of carrier gas at 38% (Figure S5c). Location of the measurement site (Figure S6). Use of exterior wall coatings, production of building coatings and completed construction area from 2000 to 2017 in China (Figure S7). Experiments of some commercial materials containing TiO_2 with a carrier gas of pure air of 66% RH and KCl concentration of 0.01 mol/L (Figure S8). Emission map of chlorine (HCl and particulate chloride) in East China (Figure S9).

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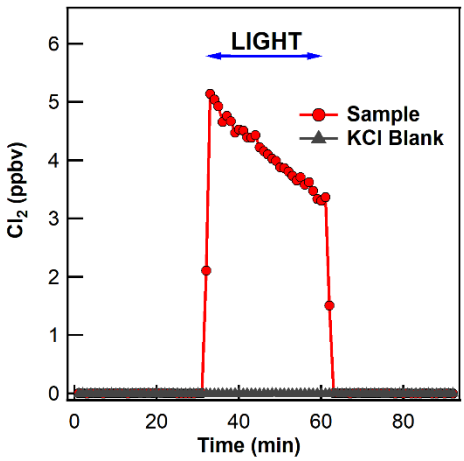
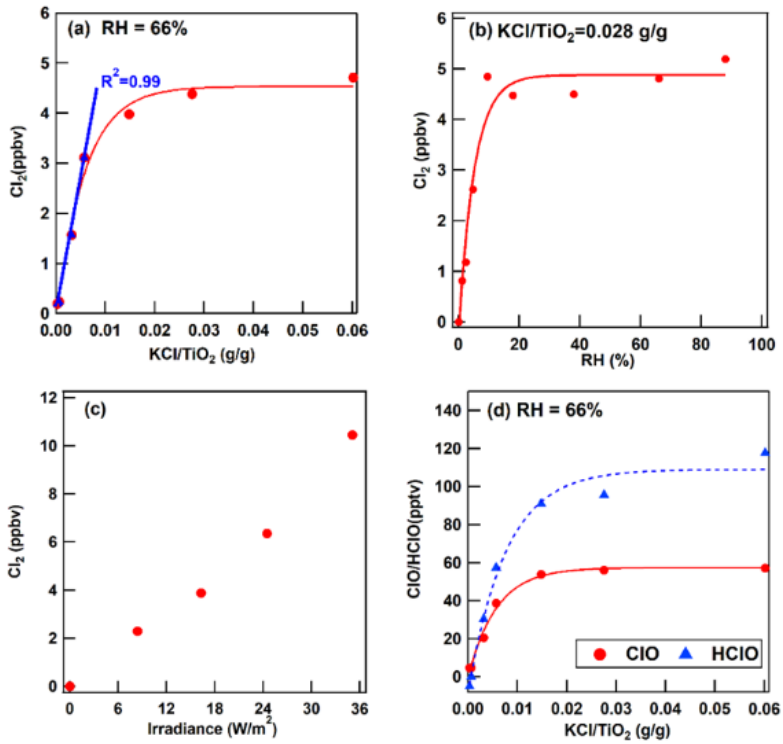


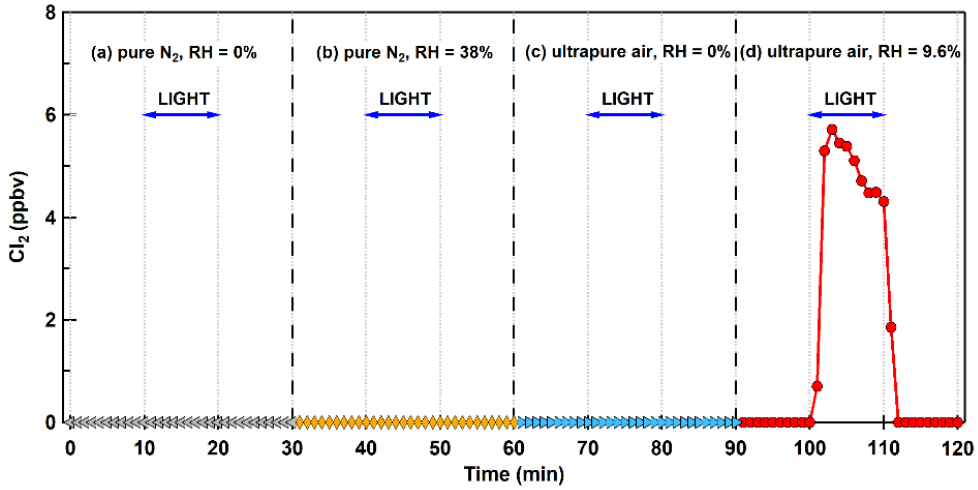
221

222 Figure 1 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)
223 on a KCl/TiO_2 (0.028 g/g) membrane using ultrapure air. The same blank signal was
224 given by a tube with a KNO_3-coated membrane.



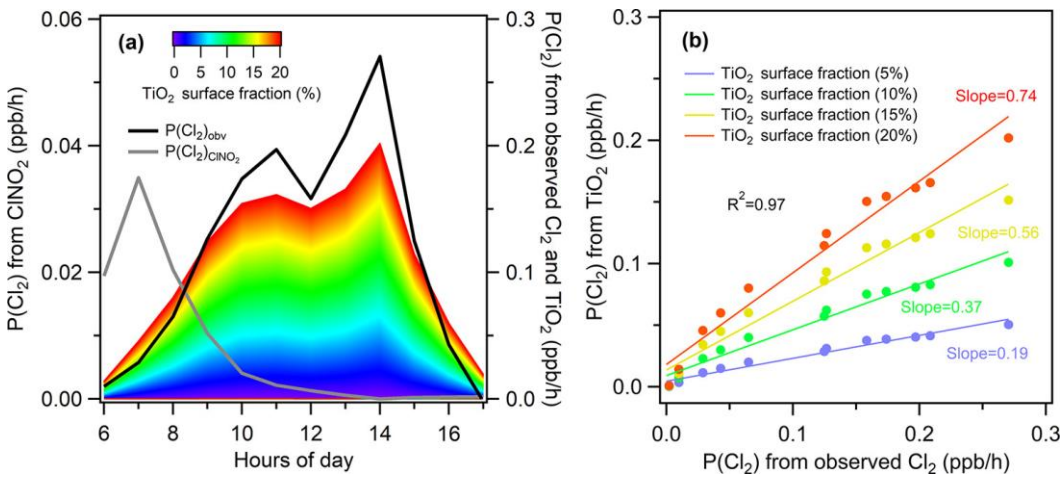
225

226 Figure 2 Dependence of the Cl_2 concentration as a function of (a) the amount of coated
227 KCl, (b) the RH of the carrier gas, and (c) the light irradiance. (d) dependence of the
228 ClO and HClO concentration as a function of the amount of coated KCl. The RH of the
229 carrier gas was 66% in experiment (a) and (d); a sample with KCl/TiO_2 = 0.028 g/g was
230 used in experiment (b); and the light irradiance is represented by the number of lights
231 in experiment (c). Red circle are all data points; red line is the fitting curve; blue triangle
232 are the first four data points, and blue line is a linear fit of these first 4 data points.



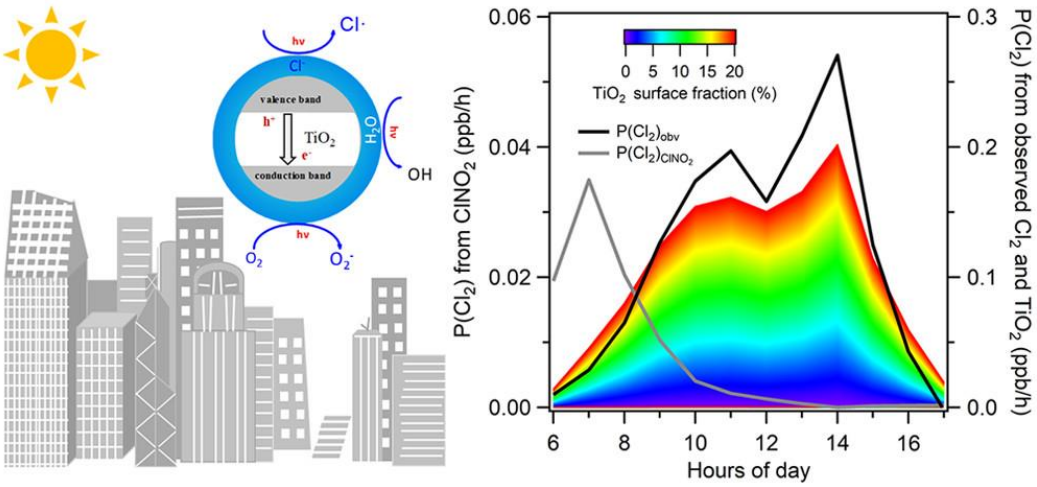
233

234 Figure 3 Effect of light (2 near-UV-emitting lamps in the 350-400 nm wavelength range)
235 on a KCl/TiO_2 (0.028 g/g) membrane with a carrier gas of (a) pure nitrogen with an RH
236 of 0%, (b) pure nitrogen with an RH of 38%, (c) ultrapure air with an RH of 0%, and
237 (d) ultrapure air with an RH of 9.6%.



238

239 Figure 4. (a)Diurnal variations of Cl_2 production rate from photolysis of $ClNO_2$, the
240 TiO_2 involved processes, as well as ambient Cl_2 diurnal variation. Filled area represents
241 a range of Cl_2 from TiO_2 photocatalysis with the assumption of 0% - 20% of the land
242 surfaces covered by TiO_2-containing materials in urban Shanghai. (b)The correlation
243 between Cl_2 production rate from Cl_2 observed data and that from TiO_2 involved
244 processes when the cover factor is 5%, 10%, 15% and 20% respectively.



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246 For Table of Contents Only (Abstract Graphic)

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